

Nov. 1, 1966

E. KAY

3,282,816

PROCESS OF CATHODE SPUTTERING FROM A CYLINDRICAL CATHODE

Filed Sept. 16, 1963

3 Sheets-Sheet 1

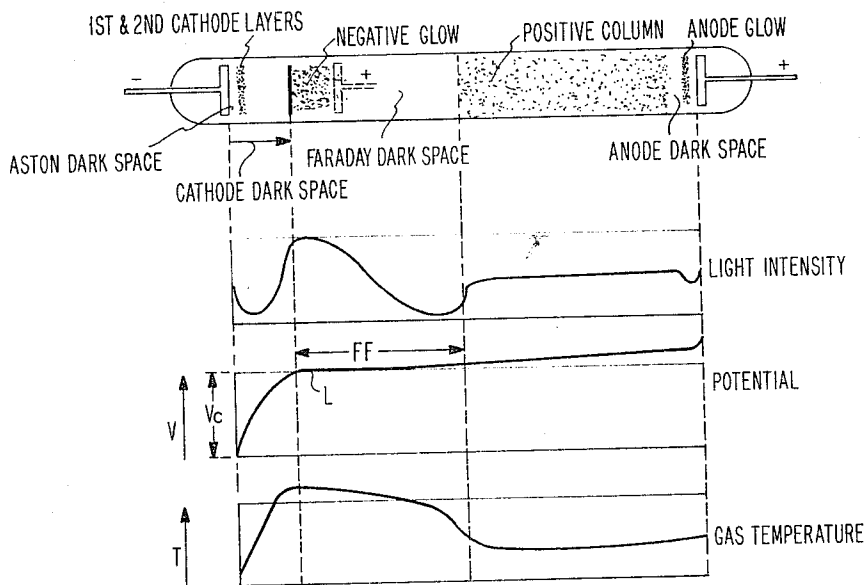
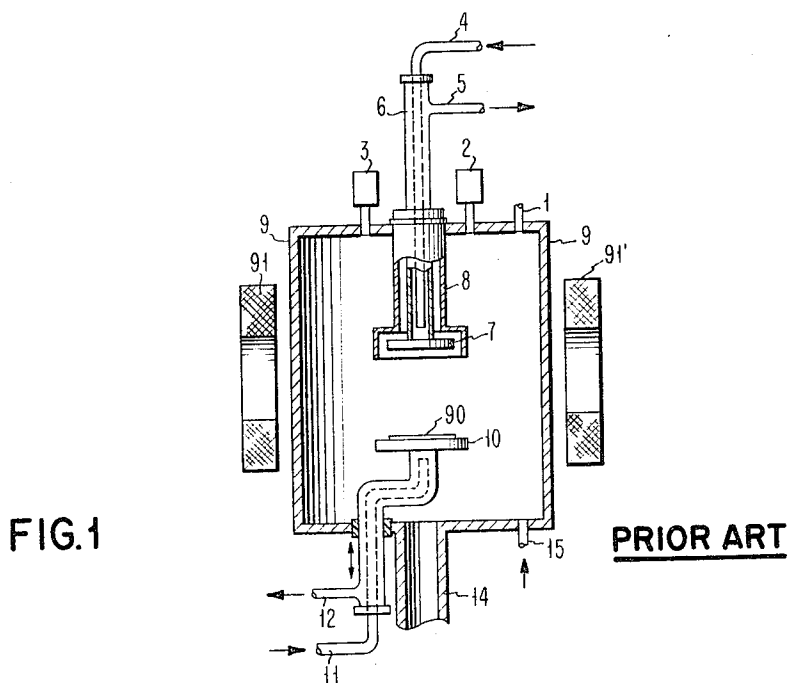


FIG.2

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3 Sheets-Sheet 2

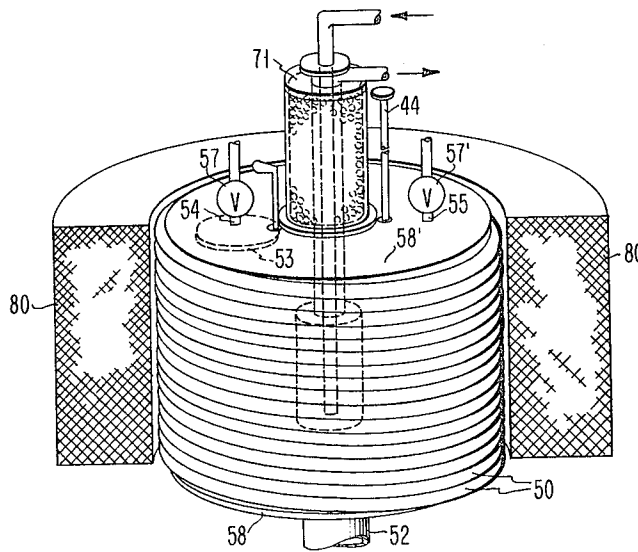


FIG. 3

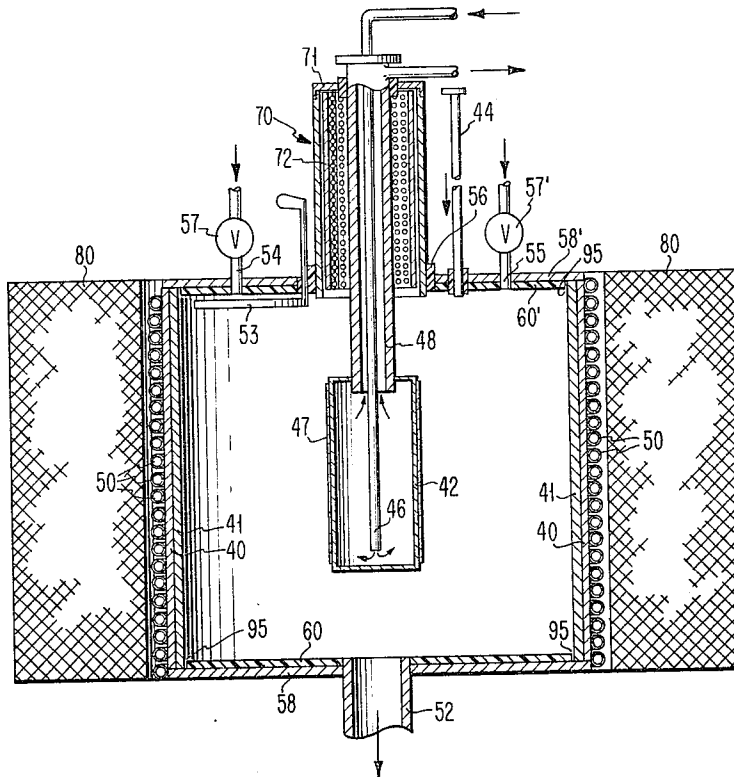


FIG. 4

PROCESS OF CATHODE SPUTTERING FROM A CYLINDRICAL CATHODE

Filed Sept. 16, 1963

3 Sheets-Sheet 3

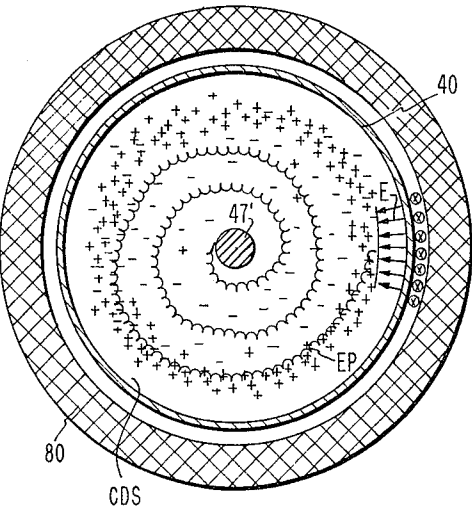


FIG. 5

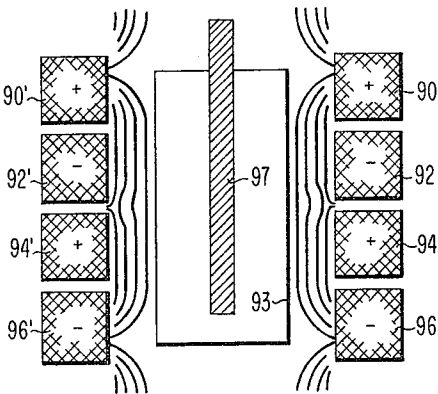


FIG. 6

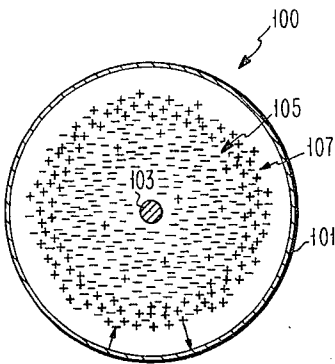


FIG. 7
PRIOR ART

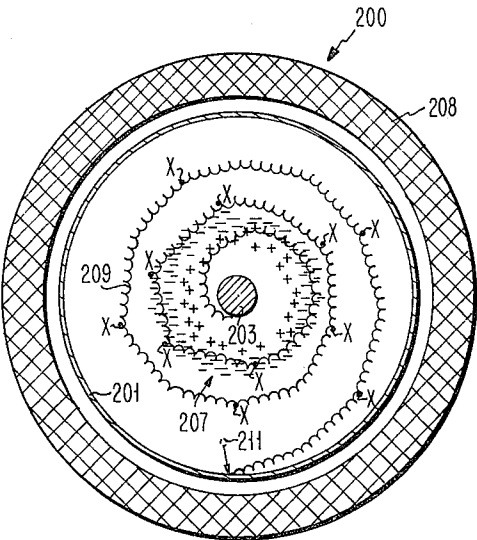


FIG. 8

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**PROCESS OF CATHODE SPUTTERING FROM A
CYLINDRICAL CATHODE****Eric Kay, Campbell, Calif., assignor to International
Business Machines Corporation, New York, N.Y., a
corporation of New York****Filed Sept. 16, 1963, Ser. No. 309,159
5 Claims. (Cl. 204—192)**

The present invention relates to improved methods and apparatus for depositing thin films of material which have been impact-eroded from a cathode, and more particularly, to such apparatus wherein the arrangement of electrodes and associated magnetic field means is such as to increase the deposition efficiency of the device, especially at ultra-low pressures, and provide closer control over sputtering processes.

Problems in the art

Techniques of depositing thin films are becoming increasingly important. One reason is for the study of phenomena which may be controllably generated in such solid-state microcosms. Such phenomena are finding increasing application in magnetic and electronic devices. Attendant upon this interest in films, giant strides forward have been made recently in the art of depositing thin films and, more particularly, in techniques for very finely controlled deposition-control over such things as purity, crystalline structure, etc. Sputtering, or impact evaporation deposition, offers promising superiority for controlling such thin film deposition from several aspects. However, in its present state, sputtering presents some problems of deposition efficiency and practical workability. For instance, although it is highly desirable to sputter thin films in a very low pressure environment (for instance, 10^{-3} to 10^{-8} Torricelli), deposition efficiencies at these lower pressures are commonly poor. The present invention radically increases sputtering efficiency and the rate of thin film deposition by several orders of magnitude, providing adequate rates at pressures as low as 10^{-6} Torr. Workers in the art will recognize that this new capability opens up new sputtering horizons in such active areas as superconductive film production.

Also important is the problem of electron-path length since the deposition rate is a function of the cathode erosion rate which, in turn, is a function of the ionization rate, and this ionization is dependent upon the length of the electron path. The present invention resolves much of the difficulty here by providing for a novel means of extending the effective interelectrode path (and hence increasing sputtering efficiency) without enlarging the interelectrode spaces.

The present invention provides a solution to the above problems and offers advantages over prior art sputtering systems according to a novel sputtering apparatus wherein a novel cathode configuration is specified; wherein a novel magnetic field arrangement is specified; wherein a novel interrelation of electrodes and field-producing means is specified; wherein a novel arrangement of auxiliary removable electrodes and associated auxiliary chambers are provided; and wherein novel uniform edge plates are provided for field uniformity at the axial ends of the sputtering vessel.

Hence, it is an object of the present invention to provide sputtering devices for efficiently producing homogeneous thin films at low pressures; for instance, on the order of 10^{-4} mm. Hg or lower.

Another object of the invention is to provide improved impact-evaporation devices having a cylindrical cathode wall and balanced magnetic field-producing means.

Another object is to radically increase sputtering rates

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by combining cylindrical electrodes and transverse magnetic fields.

Still another object is to provide a sputtering device having reduced interelectrode distances along with improved sputtering efficiencies by combining a hollow cathode device with quadrupole magnetic field-producing means.

Yet another object is to provide a sputtering device without field distortion and edge effects by providing conductive end plates therein.

Yet another object is to reduce the volume of the sputtering device and attenuate the length of the discharge zones by providing a hollow cathode sputtering device in combination with a balanced axially-symmetric magnetic field-producing means.

The foregoing and other objects, features and advantages of the invention will be more apparent and better understood from the following, particular description of a preferred embodiment of the invention as illustrated in the accompanying drawings, wherein:

FIG. 1 is a cross-sectional, schematic view of a typical prior art sputtering device with planar fixed electrodes, as opposed to the cylindrical removable electrode elements of the inventive sputtering device;

FIG. 2 is a schematic representational graph plotting the variations of glow discharge parameters and the location of glow discharge zones along the length of a typical planar sputtering discharge;

FIG. 3 is a schematic perspective representation, partly broken away, of a sputtering device according to the invention showing the disposition of the magnetic coils relative to the electrodes;

FIG. 4 is a perspective sectional view of a complete sputtering apparatus embodiment according to the invention;

FIG. 5 is a schematic, sectional view of a device such as that shown in FIG. 4 illustrating the effects of the invention upon the discharge zones and the paths of the ionized electrons under high pressure conditions;

FIG. 6 is a perspective sectional view similar to that of FIG. 3 with alternative magnetic field means illustrated;

FIG. 7 is a schematic representation similar to FIG. 5 showing discharge parameters under hollow cathode lamp conditions; and

FIG. 8 is a representation showing discharge parameters similar to FIG. 7 for the cylindrical sputtering according to the invention under high vacuum conditions.

The problems solved and the advantages achieved by the invention over the prior art are better understood by reference to the typical prior art sputtering device of FIG. 1 where a typical prior art glow discharge system is shown having planar electrodes in a single, unbalanced magnetic coil as opposed, for instance, to the hollow cylindrical electrodes and quadrupole balanced coil array of the invention as shown in FIG. 4.

The state of the prior art

Here, the glow discharge apparatus is confined in a vessel 9 which is pressure-resistant so as to accommodate evacuation to low pressures. Vessel 9 may be composed of a ceramic, or alternatively, a metal so as to readily distribute an electric charge. This vessel 9 comprises a glass envelope wherein the walls are at least two inches from the perimeter of the anode. In magnetic thin film sputtering work, the smallest diameter envelope compatible with this requirement would be used in the case where a uniform magnetic field in the plane of the film must be produced by very large (e.g., 30" I.D.) Helmholtz coils 91, 91' mounted externally of the envelope. It is vital that these coils be close to the envelope since the field degenerates with the square of the distance from the dis-

charge area. These coils are arranged to produce a field uniform to 0.1% over 6" sphere.

The cathode 7 of this two-electrode glow discharge apparatus is planar and made of the material to be transported, i.e., deposit material. However, it may, optionally, be merely overlaid with a sheet of the depository material, the basic configuration of the cathode being kept standard. The flat, planar substrate 90 is affixed upon the face of planar anode 10. Anode 10 is, of course, adjustable in the cathode-anode axial direction so as to allow a change of location of the substrate mounted thereon. The only limitation as to joining substrate 90 to anode 10 is that the connection should provide good thermal conduction. Anode 10 may be of any conductive, heat resistant metal, such as aluminum. For magnetic film sputtering the anode 10 must be nonmagnetic. Both cathode and anode are water-cooled so that their temperatures can be maintained as low as room temperature if desired. Cooling units are provided in jacket form within the base 6 of the cathode 7 and also within the anode 10. Any suitable coolant such as water may be pumped in at cathode inlet 4, emerging at outlet 5 to be cooled and recirculated. Likewise, inlet 11 and outlet 12 provide the coolant for the anode 10. The cathode-anode potential drop can be varied between 0-500 ev. using a 5 kv.-500 ma. low impedance filtered D.C. power supply. Desired glow discharge effects occur conventionally in the pressure range of 10^{-1} to 10^{-3} mm. Hg. But, in order to maintain a glow discharge in lower pressure regions, where the mean-free-path of electrons is large, the ionization efficiency has to be increased in several ways. One way is by superimposing a suitable field on the discharge and thereby increasing the effective path of the colliding electrons and hence increasing the probable number of bombarding particles generated by these collisions. The invention prescribes a novel such field for cylindrical electrodes as taught below, thereby allowing practical sputtering to as low as 10^{-8} Torr.

A diffusion pump (not shown) is used to pump down to glow discharge pressures and thereafter maintain constant pressure while clean gas is being fed in at port 15. Ion current density is very sensitive to small pressure fluctuations; therefore, the flow rate of inert gas through the system must be closely regulated.

The glow discharge zones may be contained in this configuration (FIG. 1) by the use of both an external, longitudinal magnetic field means (not shown) and of appropriately charged and shaped shielding means. Such a shielding means 8 is shown in FIG. 1 surrounding cathode 7. When placed around planar cathode 7, shield 8 facilitates discharge normally from the cathode face, toward the anode 10. The anode 10, whose configuration is not critical, can be placed at varying distances from the cathode within the range, for instance, of 4-14 cm. but beyond the "shadow zone." It should be as close as possible to cathode 7 for efficiency. The cathode cross-sectional area, however, should be at least as large as the substrate to assure maximum efficiency, as substrate 90 shows. Particular electrode areas, as related to sputtering efficiency, are recited below. The common glow discharge characteristics (e.g., current, pressure, voltage and geometry) are interrelated by well established similarity laws. Such laws are explained, for instance, in the Encyclopedia of Physics, edited by E. Flugge (Springer-Verlag, Berlin, Germany, 1956, vol. 22). These zones and parameters reflecting this are schematically plotted in FIG. 2.

Glow discharge characteristics

Now the typical glow zones and particle interaction will be described for the prior art planar electrode case, the prior art hollow cathode lamp case and the inventive cylindrical cathode sputtering case. This should facilitate a better understanding of the terminology and of the features characteristic of the prior art and thereby provide

a better appreciation of the distinctions implicit in the invention.

The prior art planar electrode sputtering case (e.g. FIG. 1 device) provides a starting point for understanding glow discharge or sputtering phenomena.

FIG. 2 schematically shows the variation of glow discharge characteristics along the length of the cathode-anode discharge for a typical planar glow discharge such as in FIG. 1. This diagram and the following description may serve to clarify some of the terms used in the instant case. A glow discharge in these configurations will take place only in a pressure range of between 1 and 200 microns Hg, though lower pressures are possible in the presence of magnetic fields. The glow discharge is maintained by electrons produced at the cathode as a result of positive ion bombardment, which electrons, in turn, will be driven towards the anode, thereby producing more positive ions to bombard the cathode, eroding particles therefrom. These particles then diffuse toward the substrate and deposit thereon. In the Aston Dark Space, there is an accumulation of these electrons which gain energy through the Crookes Dark Space, also called cathode fall or cathode dark space. The decay of excitation energy of the positive ions on neutralization gives rise to the cathode glow. The electrons which have passed through the Crookes Dark Space enter a constant-field region, some of them with fairly high velocities. This is the Negative Glow region. Here they lose their energy in further inelastic collisions in which some of them cause ionization and excite atoms, thus causing the "negative glow." The end of Negative Glow corresponds to the range of electrons with sufficient energy to produce excitation. Beyond this, in the Faraday Dark Space, the electrons once more gain energy. The Positive Column is the ionized region that extends from the Faraday Dark Space almost to the anode.

A reduction in pressure causes the cathode dark space to expand at the expense of the Positive Column because electrons must now travel farther (mean-free-path is greater) to produce efficient ionization. This phenomenon shows that the ionization processes in the cathode dark spaces are essential for maintenance of the discharge. The Positive Column merely fulfills the function of a conducting path between the anode and Negative Glow region. For the discharge to be maintained, an electron must, in its passage through the gas, produce that number of positive ions which, on striking the cathode, will release a new electron. If this self-sustaining condition is not met, the cathode dark space will expand until it contacts the anode-electrode, at which point the discharge will be extinguished.

It will be noted that this planar configuration uses only an "abnormal truncated" type of glow discharge. Such a discharge is called "truncated" because the "Positive Column" and "Faraday Dark Space" regions of FIG. 7 are eliminated and all the discharge sustaining activity occurs in the Negative Glow and Crookes Dark Space regions. It is called "abnormal" because the discharge is confined to the voltage dependent, high current region on the voltage-ion current curve.

A further explanation of typical glow discharge parameters and of the operation of planar sputtering devices may be had from copending U.S. application Serial No. 290,794 to Eric Kay, entitled "Deposition of Thin Film by Impact Evaporation" and application Serial No. 291,736 to Eric Kay and Arthur Poenisch, entitled "Magnetic Control of Film Deposition," both having an assignee in common with the present case.

Before describing the details of the inventive sputtering control techniques, it is useful to consider the parameters whereby their effectiveness is measured. One such parameter, and an important gauge of sputtering success, is "film-thickness-profile." The comprehensive nature of this parameter as an analytical tool for testing the uniformity of several film growth parameters makes it one

of the most useful criterion of film growth. On a homogeneous substrate surface with no temperature gradients, areas of uniform film thickness qualitatively indicate uniform rate of arrival of incident particles leading to uniform particle size and shape distribution in the resultant film, as well as crystallographic uniformity. Control over these parameters is especially important in the study of magnetic properties, as well as for producing films.

In almost any commonly used glow discharge device, the thickness profile on a substrate will depend on a control of the transport mechanism of sputtered particles from the source (cathode) to the substrate.

The experimentally measurable quantities upon which the film thickness profile will depend are:

- (1) The ion energy, current density, direction of ion incidence and resultant erosion profile at the cathode surface;
- (2) Substrate location;
- (3) Magnitude of the cathode fall potential;
- (4) The pressure and subsequent mean-free-path of sputtered particles; and
- (5) Proximity of the envelope walls with respect to the substrate.

These parameters above are all related to one another, and a variation of any one of them will reflect itself in the thickness profile at the substrate in a logical fashion.

To facilitate understanding and distinguishing the invention, it will now be compared to the somewhat similar hollow cathode discharge (HCD) lamp of the prior art. In the HCD device a glow discharge is modified to exhibit Negative Glow Illumination, so as to act as a lamp. Negative Glow lighting results when a plurality of opposed glow discharge cathodes are made to create discharge zones having overlapping Negative Glow regions. Illumination derives from the production of photons at this overlap region. Such a phenomenon occurs as a result of particle excitation (e.g., argon particles) to excited energy levels sufficient to allow release of photon quanta of energy (h.v.), i.e., spectral radiation. This is radically different from the function of the electrons in the sputtering environment whereby electrons are induced to ionize particles which, in turn, are made to erode a cathode surface. This sputtering mechanism would be extremely destructive in the lamp device, and hence has heretofore been carefully avoided. Such an HCD lamp is shown in FIG. 7 wherein the cathode 101 may be observed to comprise opposed cathode surfaces, here in a continuous cylindrical form. Here, when HCD conditions are invoked between cathode 101 and anode 103, opposed HCD regions will appear and produce the required overlapping Negative Glow region, schematically indicated at 105.

Of course, one might modify the structure, the purpose and the conditions of lamp 100 to change the hollow cathode type glow discharge into a sputtering discharge, although no one in the prior art appears to have suggested any practical means of doing this. To do so would require a reversal of the whole philosophy of the HCD, which necessarily involves doing everything possible to avoid sputtering since this erodes the cathode, coats tube surfaces, and thus shortens the life of the lamp. Radical changes would also have to be made in the applied voltages (raised from less than 100 to many thousands of volts), in the operating pressures (lowered for useful, pure-film production from about 1 Torr to below 10^{-5} Torr) and in increased size (for practical film dimensions, from about a cm. to the order of 100 cm.). If such typical sputtering conditions were applied to the lamp 100, they would characteristically give rise to a positive "space charge" cloud 107 adjacent the cathode 101. This cloud of particles occurs in all ordinary sputtering discharges and results from the difference in mobility of the fast electrons and the slower bombarding ions, the electrons traversing the discharge zone between anode and cathode much faster than the ions.

However, such a glow lamp condition may be modified, I have discovered, to create a new, advantageous kind of sputtering mechanism. By adjusting the pressure, the size and the voltage of the hollow cathode device as indicated above, I have learned that as long as an overlap of Negative Glow zones is maintained, sputtering may be more efficiently performed over an extended range of pressures. This condition involves photo-emitted, secondary-electron induced sputtering in addition to the usual ion bombardment secondary electron induced sputtering. Here, the Negative Glow overlap generates photons, as stated, and these in turn induce secondary photo-emission of electrons in great numbers from the cathode surface. These photo-emitted electrons thus greatly increase the number of electrons available for ionizing particles. This in turn increases the rate of sputtering and, thus, of deposition. Hence, the invention teaches a new mode of sputtering in a cylindrical cathode at higher pressures (10^{-4} Torr and up) by invoking a sputter discharge having overlapping Negative Glow regions.

Having described a "sputter-lamp" 100, we may turn to the magnetic field embodiment 200 in FIG. 8 and readily perceive its distinctions and additional advantages, especially at lower pressures where the lamp mechanism disappears (10^{-4} Torr or less). As discussed in regard to FIG. 7, glow discharge conditions will be invoked (low pressure, high voltages, etc.) as is known in the art between anode 203 and cathode 201. However, a transverse magnetic field means, such as coil 208, is also provided according to the invention to modify the discharge by superposing a uniform magnetic field transverse to it. This causes, among other things, a "double-spiralling" of ionizing electrons, radically lengthening their effective cathode-to-anode path (longer transit time—cf. FIG. 5) and thus decreasing their effective mobility. Now the transit time for electrons is longer than for the ions. This reduced electron mobility results in a reversal of the space charge from a positive charge adjacent the cathode as in FIG. 7 (zone 107) to a negative space charge adjacent the anode, as zone 207 indicates. This reversal occurs below 10^{-4} Torr pressure with the inventive magnetic field. Workers in the art may readily infer what radical changes this works in the make-up of the sputtering discharge since this electron cloud 207 comprises a "virtual cathode" and effectively moves the cathode 201 (at least electrically) to region 207. These changes are not wholly understood as yet, but superposing the magnetic field evidently attenuates some discharge regions and, furthermore, at lower pressures creates the negative space charge adjacent the anode.

Ionization efficiency increases also are achieved and derive from a conservation of electron energy. This results from the field-induced spiral recirculation of electrons (e.g., 209) through the ionization regions again and again (cf. FIG. 5) for likely multiple ionizing-collisions. The erosion increases also follow from the reduced likelihood of bombarding ions (e.g., 211) inelastically recolliding with other particles in the space charge and being prevented from eroding the cathode since the cloud no longer intercepts their bombarding path.

Of course, the intensity of the magnetic field must be maintained high enough to induce the double, or re-entrant, spiralling of the electron (e.g., 209 in the indicated path in FIG. 8). As shown, this path spirals about anode 203 as well as about itself. A field of about 700 gauss has been found satisfactory for this, in practice. The spiralling inward, toward the anode 203, results mostly from the loss in kinetic energy resulting from collisions (indicated as X).

A second constraint upon the magnetic field strength is that it must be high enough, at the operating pressure, to keep discharge regions compressed sufficiently so that, in expanding with decreasing pressure, they do not extinguish the discharge. This expansion is a function, in-

versely, of operating pressure; hence, the lower pressure, the greater the field strength must be. At 10^{-3} – 10^{-4} Torr pressure, for instance, about 700 gauss has been found adequate, using devices like that in FIG. 4.

Thus, the provision of a magnetic field upon a sputtering discharge in a cylindrical cathode according to the invention both increases electron paths and attenuates discharge zones.

An exemplary embodiment

With the above understanding of the characteristics and operation of the glow discharge mechanism both in the prior art and with the invention, one may better appreciate the significant changes inherent in the cylindrical cathode discharge array of the invention and the advantages achieved by the electrode-field interrelation specified, according to the invention, in the following embodiments.

One embodiment suitable for practicing the invention is the sputtering device shown in FIG. 4. It is important to note here that according to the invention the vessel chamber takes the form of the cylindrical cathode 40 itself. This is a radical improvement over all forms of prior art sputtering devices, since it simplifies structure, saves parts and space and allows the cathode to be conveniently cooled with external means, for instance by coils 50, in thermal-transfer relations with cathode 40. Coils 50 are filled with a conventional coolant, such as water or liquid nitrogen, and operate to cool the ion-bombarded cathode so as to maintain it thermally stable. However, any alternative cooling means may be used. The point is that whatever means is used, such a combination "cathode-container wall" array will present a greatly simplified cooling problem. Convenience is enhanced especially because the cathode is no longer lodged within an evacuated envelope as in prior art devices, requiring that the cooling means be introduced in an evacuated enclosure and enlarging the enclosure volume, all of which contribute towards a great many evacuation and sealing problems. Additionally, and more significantly, this cathode-wall feature allows the field coils (e.g., coils 80) to be conveniently located much closer to the electrodes and the discharge itself, conserving field strength.

Substrate 47, which is the article to be coated, is positioned within the chamber formed by cylindrical cathode 40 and, when sputtering conditions are invoked, will be sputter-coated with the material eroded from cathode sleeve 41 within cathode 40. The sputtering glow discharge condition is applied between substrate 47, which is ohmically connected to the positively charged anode 42 and the inner surface of sleeve 41, of course. Alternatively, the surface of the cathode 40 may be directly eroded by removing sleeve 41, which is only provided for convenience and versatility. As in any sputtering atmosphere, the eroded material effectively "fills" the discharge chamber with a "gas" having the same composition of sleeve 41 (even if it is a multicomponent alloy). This gas diffusively emanates toward, and deposits itself upon, the surface of substrate 47 in a uniform, carefully controlled manner. One especially attractive feature of this novel sputtering arrangement is that, with such a cylindrical cathode configuration, depository material can be made to uniformly and more efficiently deposit itself over the surface of any shape substrate. This is because the cylindrical cathode of the invention produces omnidirectional deposition, as opposed to the unidirectional mode in planar cathode devices. For instance, a charged prism may be placed within the cylinder in place of substrate 47 and anode 42 and be sputter-coated uniformly without significant dependence upon its shape or position. Uniformity will be optimized if it is rotated as well. This is a radical and significant difference over prior art glow discharge devices which are extremely position-dependent, and the shape of whose substrates is necessarily quite fixed. Further, if there is suffi-

cient room within the cathode (the invention enables one to use larger and longer cathode arrangements), it will be evident that more than one such article of varying shapes and positions may be simultaneously mounted in axial array within the single, cylindrical cathode; the only constraint being that there be no blocking surface between such an article and the eroding surface of the source-sleeve 41. It will be evident to those skilled in the art, of course, that sleeve 41 of depository material may comprise any suitable material to be deposited on the substrate 47, as long as it is ohmically and thermally connected to cathode 40. This allows a convenient change in deposition source-material. Of course, the source-material might comprise the cathode cylinder itself, although it would be preferable not to erode this, keeping it uneroded to serve as a container wall. Likewise, substrate 47 might alternatively comprise the anode 42 itself which may be introduced axially of the cathode wall through chamber 70. However, it will be evident that it is more convenient, where possible, to use an inner anode surface so as to provide a constant medium for introducing the object, as well as a constant means for cooling it. Alternatively, anode 42 might comprise a slide-holder of any convenient shape, for instance, a prism. Such a prism might be provided with slide-engaging insets to engagingly mount the slides while in the discharge chamber or such equivalents as will occur to workers in the art. Cooling is performed conventionally within the structure of anode 42 by introducing a coolant, for instance, through conduit 46, the heating of which will cause it to exit through outer conduit 48. However, any convenient coolant system evident to those skilled in the art may be substituted for this. It will be apparent that auxiliary chamber 70 in conjunction with its removable top 71 provides an access port through which the anode substrate configurations may be axially inserted, allowing for instance for the substrate 47 to be introduced quickly and easily into the chamber and thereafter removed. A second, and wholly unobvious, function of chamber 70 is for clean-up purposes. Such a precleaning arrangement is aided also by the novel elements comprising rotatable shutter 53, grid 72, and auxiliary anode 44, the latter being axially removable.

The novel precleaning technique using these elements is as follows.

With the substrates positioned in the auxiliary chamber 70 and shutter 53 rotated so as to close off this chamber from the main apparatus, auxiliary anode 44 is introduced into the main discharge chamber and charged to sputtering potential, so as to initiate clean-up sputtering (or erosion) of the inner vessel walls within the chamber. The clean-up material may be captured either by depositing it upon auxiliary anode 44 or by pumping down during sputtering through port 52, evacuating the eroded clean-up material. Such precleaning by ion bombardment lends itself particularly to the apparatus of the invention, as here described. The provision of the auxiliary anode 44 makes it unnecessary to remove or cover the substrate during clean-up discharge time.

A second clean-up operation may be performed upon the substrate objects while in the auxiliary chamber 70. Perforated grid 72 is provided for this purpose and, during clean-up, is charged with respect to the substrates so as to bombard the substrates with low energy (about 300 ev.) ions ("Canal Ray" bombardment) passing through the electrode perforations. In this configuration, electrons will be repelled by the perforated grid 72, keeping the substrates out of the high electron density plasma to avoid electron-induced contamination, e.g., polymerization of oil vapors. Then, after suitable precleaning by ion bombardment, the substrates can be introduced into the sputtering chamber for coating.

It may be noted in connection with auxiliary chamber 70 that it is sealably but insulatedly connected, for in-

stance, by Teflon insulation 56, to the end plates 58, 58' of the main chamber.

End plates 58, 58' are provided as the axial closures of the container formed by cylindrical cathode 40. These end plates are made of a metallic material, preferably the same material as cathode 40 so as to extend the effective cathode surface electrically, preventing undesirable sharp field gradients at the cylinder edges. Sheets 60, 60' of dielectric material overlie the outer surfaces of end plates 58, 58' entirely, except for gaps 95 (of a few mm.) adjacent sleeve 41. This obstructs the discharge at the end plates, thereby preventing erosion thereof and still avoids a metal-to-dielectric vacuum seal by allowing use of metal closures 58, 58'.

Valves 57, 57' are provided in the entry ports 54 and 55 for controlling the amount of inert gas admitted to the sputtering chamber. Such valves are preferably provided with controls to enable them to act as a variable-leak gas input so that input gas may be continually admitted in minute amounts to flow into the discharge space and thereby cool the substrate 47 during the cathode sputtering period. If necessary, such an auxiliary cooling means can provide the same advantages as the anode cooling means 45, etc. Control of the substrate temperature is, of course, important because it affects both the physical properties and chemical composition of the sputtered film deposited thereon. This temperature becomes especially critical when oxidizable materials are sputtered or when the sputtered film is to be magnetically oriented during deposition. Without control of the substrate temperature sputtering, so as to maintain uniformity of physical and chemical properties in the deposited layers, is virtually impossible. Also, thermal vaporization of cathode material must be prevented, for example, so that an alloy constituent would not be evaporated rather than sputtered. These are important reasons for cooling the cathode carefully—something the inventive "cathode-wall" 40 facilitates.

Thus, the invention is seen to provide a new electrode configuration leading to novel discharge characteristics, and includes a cylindrical cathode-wall, removable electrodes, auxiliary discharge chamber and equipotential but nonsputtering end plates for improved sputtering.

The field arrangement

Besides teaching the structural changes noted above, the invention also provides a novel field arrangement. It will be observed that a magnetic field-producing coil 80 is provided in FIG. 4 surrounding the sputtering chamber. Coil 80 may be substituted for by any equivalent means for generally providing an axially transverse magnetic field, directed axially of the chamber formed by cathode 40 and radially symmetric therealong, according to the invention. This novel field means coacts with the cylindrical electrode arrangement of the invention and is a new and unobvious improvement over prior sputtering apparatus, yielding an increase in sputtering efficiencies on the order of 10 to 100 times, depending upon the sputtering conditions. Such efficiency increases are vitally important in the art, making sputtering more competitive with deposition rates of other methods and practical at lower pressures. The imposition of the magnetic field, as prescribed by the invention, tends to increase the degree of ionization, subsequently increasing the cathode erosion rate and, in turn, the deposition rate. One vital reason for this is exemplified in FIG. 5 which generally shows a cross-section through the sputtering device shown in FIG. 4, illustrating the relation of the cathode 40, the anode-substrate combination 47', the Crookes Dark Space (CDS), and schematically, a typical electron path EP from cathode-to-anode. This schematically demonstrates how the electron path length is increased by the imposition of the magnetic field (lines X), proceeding unidirectionally and axially of the cathode 40 (into the paper). The re-entrant spiral path EP is in-

duced by the interaction of the magnetic field emanating from coils 80 with the electric field E between the electrodes (about 2,000 electron volts between the anode and the cathode material). Field E proceeds radially between cathode 40 and anode-substrate 47'.

As best understood, there are at least two cooperating effects from the superposition of this magnetic field upon the device. One effect is to attenuate, or shorten, the length of the glow discharge zones (for instance, the Crookes Dark Space) and thereby allow the interelectrode gap to be reduced. This allows the sputter device to be decreased in volume, as well as increasing the density of ionizable material by attenuating the ionizable zone. As schematically illustrated in FIG. 5, the other result is to induce the helical re-entrant spiralling path EP of the electron as it proceeds to the substrate-anode 47'. This spiralling occurs both about the anode itself, as well as about the longitudinal path of the electron, and hence, is a re-entrant or double-spiralling. It will be evident that the result is to greatly elongate the effective path of the electron and thus to increase the probability of its producing an ionizing collision. This, in turn, increases the ionizing efficiency of the system so that the bombarding, or erosion, rate upon the cathode is enhanced, along with an enhanced deposition rate resulting therefrom. Improved efficiency also results from the fact that, due to the cylindrical cathode arrangement, the particles sputtered from the cathode are almost 100 percent utilized and little cathodic material is wasted. This is because the eroded material must either strike the substrate or continue its diffusive migration until striking a cathodic surface surrounding the substrate, from which surface it can be re-eroded. This results, obviously, in a great saving in expensive depository cathodic material, as well as in greatly reduced problems in tube clean-up, resulting from deposition upon noncathodic, nonsubstrate surfaces. The saving is apparent from considering planar electrode devices (e.g., FIG. 1) wherein much material can easily be trapped on the tube walls laterally of the discharge direction.

Use of such a radially symmetric transverse magnetic field in the cylindrical cathode discharge device according to the invention, by thus increasing sputtering efficiencies, enables workers in the art to efficiently sputter at lower pressures than has been heretofore possible. For example, sputtering has been achieved down to 10^{-8} Torr, where before the invention it was impractical below 10^{-4} Torr.

Alternative field arrangements

For the situation where "edge effects" are significant, an alternative magnetic field configuration is prescribed according to the invention; namely, an axially-balanced or "quadrupole" magnetic field such as that shown in FIG. 6. Here, the cylindrical cathode discharge configuration is essentially similar to that in FIGS. 4 and 5, the discharge taking place between cylindrical cathode 93 and centrally-disposed substrate-anode 97, kept for instance at a potential of about +3,500 electron volts with respect to cathode 93. As in the prior substrate configurations, anode 97 may be any commonly shaped object as long as it is somewhat parallel to cathode 93 and fits within the discharge area. The potential of the cathode 93 is essentially at ground, as before. The change here, of course, is in the provision of four magnetic field generating coils 92, 92', 94 and 94' which, as the positive and negative signs and the field lines indicate, are arranged in alternating polarity or "field opposing" relation. Such an array generates quadrupole magnetic fields which, as the flux lines schematically indicate, are transverse and radially symmetrical as in the case of the unidirectional, single coil field, but unlike it are also bidirectional and axially symmetrical and thus effect "balanced" or "bucking" magnetic fields. As indicated above, the effect of such a quadrupole or balanced magnetic field

is to eliminate the "edge effects." These edge effects consist in a deposition thickness variation at the edges of the substrate array. In these end regions, deposition is increased and thus the edge effects are produced as a result of the increased erosion rate usually encountered at the edges of the cathode because of the greater erodibility of oblique-incident ions and the steeper field gradients existing there. End plates 58, 58' described above alleviate the field gradient, of course. A bidirectional, balanced field cures this by uniformly dispersing the electrons axially. The four coils shown in FIG. 6 reduce this asymmetric erosion profile at the substrate edges, which detracts from film thickness uniformity. These coils produce a substantial magnetic field component near the ends of the cylindrical cathode which is parallel to the electric field as the schematically-indicated field lines indicate. Such a field adjustment is made by adjusting the current flow in the coils appropriately to achieve a field similar to that schematically shown in the diagram. The object, of course, is to compensatorily reduce the amount of ionization at these edges to a degree proportional to the higher sputtering rate there.

Applications of the field

It has been shown that, as a result of employing the inventive radially symmetric transverse magnetic field, workers in the art can greatly enhance ionization efficiencies and hence the efficiency of erosion and deposition using the cylindrical cathode device of the invention. Further advantages derive from balancing the field axially, eliminating edge inhomogeneities. As a result of these advantages, such sputtering devices can be used efficiently at lower pressures (for instance, about 10^{-8} Torr as opposed to about 10^{-4} Torr) than was prevalent heretofore in the prior art. This overcomes a major drawback in prior art sputtering configurations, especially for example in the production of superconducting or magnetic thin films where purity is of the essence. Such film production will now be described.

The inventive sputtering arrangement has been found practical and advantageous for depositing thin, high-grade magnetic films. Such films can be prepared with a cylindrical cathode discharge according to the invention taking advantage of the ability to grow high purity films in a very high vacuum. If very high rates of deposition are required, this can be enabled by using the transverse magnetic field at higher pressures. One might, however, wish to operate at low pressures so that collisional processes in the plasma are avoided. However, such collisions can introduce unwanted, uncontrollable reactions resulting in undesirable films. Large orienting fields can now be used without distorting the discharge if they are supplemented with the balanced magnetic field along the discharge. Care must be taken that the cathode does not extend beyond the flux path (most of the flux should extend beyond it) lest the cathode short circuit the magnetic field and remove the uniform field in the plane of the film. Loss of this transverse field in the region of the glow discharge will also prevent the enhancement of ionization and sputtering rates.

Superconductor applications

The invention may also be advantageously employed to deposit superconductor films, for example such "hard" superconductors as Nb-Zr, Nb₃Sn, V₃Ga, etc. It has already been established in the literature that it would be highly desirable to obtain these "hard" superconductors in thin film form because, among other reasons, their current-carrying capacity in the presence of the inevitable magnetic field is greater in this form than in bulk form. It is also thought that the thin film version of these materials is an essential requirement for their ability to become superconducting along "filaments" in the structure. These films naturally lend to the production of materials which must have a high density of structural defects (inhom-

geneities). Workers in the art will prefer to sputter such superconductor thin films for the following reasons:

(1) These materials are *refractory* and can therefore be readily transported from source to substrate by a momentum transfer controlled process (i.e., sputtering), but not by vaporization techniques.

(2) These alloys have constituents of *highly varying vapor pressures* so that deposition by thermal evaporation is highly impractical, while sputtering is practical.

Moreover, the cylindrical cathode device, according to the invention, should lend itself particularly well for these films because it provides:

(a) The choice of depositing in either a high pressure environment (e.g., 10^{-2} Torr) or a low pressure (e.g., 10^{-8} Torr), depending on whether the formation of structural defects or the reduction of chemical impurity sites is desired. By contrast, the prior art planar glow discharge is much less efficient and is inoperable at pressures of 10^{-3} Torr or less.

(b) One of the most desired geometries in which to obtain these hard superconductors, i.e., is in the form of a wire or ribbon so that they can be wound in magnet coils to give high magnetic fields (e.g., 10^{-5} gauss). Obviously, such cylindrical deposition is a special capability of cylindrical cathode devices. Presently, such wires cost thousands of dollars because of the difficulty in producing them. Also, some of these materials are extremely brittle, particularly Nb₃Sn and V₃Ga so that any handling, such as bending, destroys them. Also, handling often destroys the type and density of the defect-sites that cause them to be superconductive.

For more specialized applications of the invention, workers in the art may use the invention to sputter superconductors onto wires. Using an HCD according to the invention, one could coat a ductile wire whose thermal expansion coefficient is close to the desired superconductive material as a base for the magnetic coil conductors by making such wires the anode in the center of the sputtering device. The coating would be perfectly symmetrical, as desired. Temperature control of such wires might still be a problem, of course.

The substrate one chooses must not go superconducting itself, but act as a normal conductor at low temperatures. By coating superconductor wires by the inventive cylindrical cathode method, one may manipulate (e.g., wind) them easily without worrying about the brittleness of the film. Needless to say, this applies for any filaments coated according to the invention.

Other applications

As will be evident to those skilled in the art, the advantages achieved by the applicant's modification of the present sputtering apparatus makes continuous deposition of sputtering substrates more feasible, a thing heretofore impractical in the art, though much desired. The simplicity, ease of coating and miniaturization of the device achieved by the inventive cathode-wall as well as the increase in sputtering efficiency, the decrease in interelectrode distances and the improvement in film uniformity enabled by the inventive magnetic field, all facilitate this. As will be recognized by those skilled in the art, for such a continuous operation one must provide a device which coats quickly and uniformly, evacuates easily and is relatively simple.

There are at least two feasible techniques for transporting a series of articles to be coated into the cathode chamber and removing them after deposition. The articles can move continuously from outside the vacuum chamber to inside the chamber through a means that will stop any air flow into the chamber and be removed from the chamber in like fashion, for example a drop in pressure in stages. Alternatively, periodic dispensing means may be provided to insert the object, invoke sputtering and then remove the object all automatically.

Workers in the art will recognize that sputtering is useful in the fabrication of a wide variety of coated articles. The class of materials wherein the novel sputtering method and apparatus of this invention is superior to other deposition techniques includes alloys, metals having low vapor pressures, and expensive materials. The transport of alloys is impossible using vacuum evaporation techniques, except where the vapor pressures of the alloyed materials are very close together; whereas sputtering works independent of vapor pressures. Metals that are refractory or hard to evaporate, such as platinum, iridium, tantalum, tungsten, zirconium, and molybdenum, are difficult subjects for vacuum evaporation, but no problem for the sputtering deposition. Materials which are expensive, such as gold or palladium, can now be deposited by means of the present invention without the expensive waste of material characteristics of vacuum coating.

In summary, the invention provides an improved method and apparatus for depositing films by sputtering. The invention teaches how a wide variety of coating materials can be deposited with greater uniformity as to both thickness and composition. It teaches how articles may be sputtered uniformly despite an irregular surface conformation. Further, the method and apparatus provide greatly increased sputtering rates, allowing practical sputtering at much lower pressures. The invention makes such efficient use of the cathodic source material that it is less expensive to sputter costly materials. Further, the improved efficiency and economy of the invention make the adaption of sputtering for continuous, mass production techniques now more feasible.

While this invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. The process of coating an article by sputtering in a sputtering apparatus including an anode and a cathode, said cathode comprising a right-circular-cylindrical surface, said method comprising the steps of:

arranging said article such that it is disposed along the axis of said cylindrical cathode for uniform deposition thereon,

imposing within said apparatus a suitable pressure of ionizable gas and a suitable anode-cathode voltage potential difference to thereby obtain abnormal glow discharge conditions within said cathode, such that said discharge is radially symmetrical about said axis; and

superposing upon said discharge a magnetic field having a major component parallel to said axis and transverse to said discharge, said field being radially symmetric about said axis and of sufficient intensity to induce electron spiralling within said discharge and yet maintain said discharge.

2. The process of claim 1 including the additional step of:

enclosing the ends of said cathode so as to form a sealed vessel, said ends being electrically insulated from said cathode to avoid sputtering thereof, said vessel thereby forming the enclosure for said sputtering process.

3. The process of claim 2 wherein said magnetic field is of the edge-graduated axially-balanced type so as to thereby compensate for edge erosion inhomogeneities.

4. The process of claim 1 wherein said imposing step is conducted so as to cause said discharge to have one common negative glow region disposed about said axis.

5. The process of claim 4 including the additional step of:

reducing said pressure of said ionizable gas after superposing said field to a value no lower than that required to maintain said discharge.

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